Organometallics 2014 vol.33 N24, pages 7125-7134

Organolanthanide complexes supported by thiazole-containing amidopyridinate ligands: Synthesis, characterization, and catalytic activity in isoprene polymerization

Luconi L., Lyubov D., Rossin A., Glukhova T., Cherkasov A., Tuci G., Fukin G., Trifonov A., Giambastiani G.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2014 American Chemical Society. Neutral bis(alkyl)-organolanthanide complexes supported by tridentate {N-,N,N} monoanionic 5-methylthiazole- or benzothiazole-amidopyridinate ligands have been prepared and completely characterized: (LThiaMe2)Ln(CH2SiMe3)2 [Ln = Lu3+ (3), Er3+ (7), Yb3+ (8)] and (LBnThMe2)Lu(CH2SiMe3)2 (5). Similarly to related Y3+ systems, the nature of the thiazole unit controls the ultimate catalyst stability in solution. In the diamagnetic Lu3+ complex 5, a progressive and complete rearrangement of its metal coordination sphere takes place through a metal-to-ligand alkyl migration with subsequent benzothiazole ring-opening and generation of the Lu3+ mono(alkyl)-arylthiolate species stabilized by a tetradentate {N-,N,N,S-} dianionic ligand. On the other hand, the 5-methylthiazole-containing complexes 3, 7, and 8 showed no evidence of any ligand rearrangement. Complexes 3-8 have been tested as homogeneous catalysts in isoprene (IP) polymerization, after activation with selected organoborates. Binary systems 3/TB and 7/TB [TB = tritylium tetrakis(pentafluorophenyl)borate] show the highest activity and living character toward IP polymerization, affording polymers with relatively high trans-1,4-selectivity (up to 76.4%), moderate molecular weights (Mn up to 146′000 g/mol), and narrow polydispersities (Mw/Mn). Depending on the rare-earth ion of choice, a prevalent trans-1,4 (Lu3+, Er3+, Yb3+; up to 76.4%) or a dominant 3,4 (Y3+; 92.7%) polymer structure is observed. The influence of the ligand type, metal ion, and activator(s) on the ultimate catalyst activity and selectivity is discussed.

http://dx.doi.org/10.1021/om500918y